

PORTLAND HARBOR RI/FS
REMEDIAL INVESTIGATION REPORT

APPENDIX D2.3
**PATTERNS AND TRENDS OF PCBs, PCDD/Fs, DDX,
AND PAHS IN SEDIMENT TRAPS**

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APPENDIX D2.3 PATTERNS AND TRENDS OF PCBS, PCDD/FS, DDX, AND PAHS IN MOBILE SEDIMENT

D2.3.1 Introduction

This appendix provides additional details on the nature of the four grouped indicator contaminants, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs), DDX, and polycyclic aromatic hydrocarbons (PAHs), by examining the spatial patterns in the occurrence of the constituent contaminants that make up these compound groups.

D2.3.2 Patterns and Trends of PCBs in Mobile Sediment

The distribution of detected PCB homologs and Aroclors is shown in stacked bar charts in Figures D2.3-1a-b and D2.3-2a-b, respectively. The bar charts show the percent composition of individual PCB homologs and Aroclors for each sample, while the total concentration of the indicator contaminant is displayed as a line on a logarithmic scale. Station location labels are provided on the x-axis, and river mile is indicated on the secondary x-axis along the top of the chart. Station location labels are provided on the x-axis for the 2007 locations. Note that all 2009 locations are from RM 11E.

Tetrachlorobiphenyls (tetraCBs), pentachlorobiphenyls (pentaCBs), hexachlorobiphenyls (hexaCBs), and heptachlorobiphenyls (heptaCBs) were the predominant homolog groups in the sediment trap samples. Aroclors 1254 and 1260 accounted for most of the reported Aroclors, which is consistent with the homolog composition. Aroclor 1254 consists primarily of pentaCBs followed by tetraCBs and hexaCBs, and Aroclor 1260 contains mostly hexaCBs and heptaCBs (Figures D2.3-1a-b). DiCBs and triCBs were detected in most samples and are consistent with patterns displayed by weathered Aroclors 1254 and 1260.

In addition to Aroclors 1254 and 1260, Aroclors 1221 and 1242 were reported in eight instances. Aroclor 1221 was reported once, in the Quarter 3 sample from ST011 (RM 3.5E) at a concentration just above the method detection limit and with qualifiers “NJ” (i.e., tentatively identified and estimated). Aroclor 1242 was identified in seven samples from Quarter 2, all at concentrations below the method reporting limit of approximately 10 µg/kg, but was not identified during other sampling periods. Considering the low levels at which these Aroclors were detected and the regular occurrence of weathered Aroclor components among samples, it is conceivable that the partially dechlorinated PCBs in these samples led to misidentifications as Aroclors 1221 and 1242.

The higher concentrations and apparent increased dominance by hexaCBs and heptaCBs in samples from ST007 during Quarters 2, 3, and 4 (Figures D2.3-1a-b) suggests that the dominance of higher chlorinated PCBs may increase with increasing

concentrations. A covariance matrix¹ of the sediment trap data set was constructed and investigated, both graphically and quantitatively. The data were log-transformed, centered and scaled to conform to the assumptions of normality and equal variance required for the parametric correlation metric used (Pearson's R).

The congener results showed a very uniform correlation structure, indicating that the relative homolog ratios were statistically similar among all samples regardless of total concentration. All of the PCB homologs had strong (Pearson's R in the 0.9 range) and significant positive relationships throughout the entire data set (Figure D2.3-3). Only decaCBs (otherwise a minor contributor to the total PCB concentration in all samples; Figures D2.3-1a-b) had slightly lower correlations (Pearson's R in the 0.6 range) to the other nine homologs. Taken together, these results strongly suggest that across the entire range of total PCBs concentrations within this data set, the relative proportions of all 10 PCB homolog groups are essentially constant.

Four homolog groups (tetraCBs, pentaCBs, hexaCBs, and heptaCBs) clearly dominate the PCB composition of all sediment trap samples (Figures D2.3-1a-b), constituting 80 to 90 percent of total PCBs throughout the data set. Though the three samples (from Quarters 2, 3, and 4) collected at station ST007 visually appear to have slightly more hexaCBs and heptaCBs than others, quantitative analysis of these data indicates that the overall composition of these ST007 samples falls in line with the rest of the data set (Figures D2.3-3 and D2.3-4).

The relationship between PCB homolog concentrations and the calculated net deposition rate of the sediment trap samples was examined (the deposition rate data variable is coded "DEPRT" in Figure D2.3-3). None of the PCB homologs, or total PCB concentrations, was significantly correlated to the solids deposition rates in the sediment traps (Figure D2.3-3).

PCB homolog distributions in sediment trap samples were generally consistent from quarter to quarter at each location resulting in a high degree of similarity among the samples in this data set (Figures D2.3-1a-b). The PCB composition of all samples was dominated by tetraCBs, pentaCBs, hexaCBs, and heptaCBs (80–90 percent of total), but minor localized or temporal variations were also noticeable. These small-scale deviations may be indicative of potential localized sources, but also may be within the range of normal data variability. Detailed forensic analyses would be required to determine whether or not these minor variations represent statistically significant departures from the overall PCB pattern, which may be linked to local sources. Variations apparent in the stacked bar charts and a comparison of the paired sediment trap samples are discussed below:

- The sample from Quarter 1 of the 2006/2007 sampling event at ST009 (RM 15.7E) had a slight increase in the proportion of pentaCBs and hexaCBs,

¹ A regression analysis was not selected because homolog concentrations and total PCB concentrations are not independent variables, i.e., both are calculated from the same congener data set.

along with consistent contributions from tetraCBs and octachlorinated biphenyls (octaCBs). Samples at this station from the other three quarters had slightly greater contributions from diCBs, triCBs, tetraCBs, and octaCBs. ST010 (RM 15.6W) is located west of ST009, and the Quarter 1 sample from this station showed a slightly greater proportion of pentaCBs compared to other quarters, but to a lesser degree than was seen at ST009.

- HexaCBs and heptaCBs appeared to contribute increased proportions to the PCB concentrations at ST007 (RM 11.3E) as total concentrations increased in Quarters 2, 3, and 4 of the 2006/2007 sampling event. The proportion of octaCBs was also slightly higher in these samples, and the proportion of tetraCBs and pentaCBs was slightly lower, in comparison to those from upstream locations. This small-scale change in PCB pattern, combined with the high concentrations, may indicate the presence of a localized source of PCBs in this vicinity during Quarters 2, 3, and 4.² The PCBs in Quarter 1 at this location were different from the subsequent quarters, with relatively higher percentages of triCB and tetraCB fractions, relatively lower hexaCB, octaCB, and heptaCB fractions, and a much lower total PCBs concentration. However, the overall composition profile and magnitude of the total PCBs concentration at ST007 are, in fact, closer to the other samples in this data set.
- The PCB patterns at ST008 (RM 11.5W), across from ST007, appeared slightly different from ST007, and the PCB concentrations were lower; ST008 does not appear to exhibit significant influence from ST007 in terms of PCB composition.
- The PCB homolog distributions (Figure D2.3-1b) were generally similar from quarter to quarter at each location during the 2009 sampling event, as was observed in the LWG sediment trap study. The sediment traps at station ST001, the Quarter 3 sample from ST002, and Quarter 4 sample from ST003 and ST006 were predominantly hexaCBs and heptaCBs, similar to the homolog distributions seen in the LWG sediment traps at RM 11.3E in Quarter 2 through Quarter 4 as noted above. Other sediment traps exhibited higher percentages of the lower chlorinated homolog groups, primarily tetraCBs and pentaCBs.
- A small shift of the pattern of higher chlorinated PCBs was consistently seen at ST006 (Swan Island Lagoon), ST015 (RM 9.7W), and ST016 (RM 9.9E). All samples from these stations were predominated by pentaCBs, hexaCBs, and heptaCBs.
- ST013 (RM 6.7E) in Willamette Cove was composed primarily of moderately chlorinated homologs (tetra- through heptaCBs), with relatively high contributions from octaCBs in all three quarters sampled. While the PCB homolog distribution was consistent for all samples from this location, the total

² ST007 is located between two facilities with active, deep draft docks (i.e., between RM 11.3E and 11.4E).

PCB congener concentration in the Quarter 4 sample was 5 times higher than during Quarter 1.

- The pattern of the Quarter 1 sample at ST004 (RM 6.0E) appeared slightly shifted towards higher contributions of hexaCBs and heptaCBs, whereas samples from other quarters at this station more closely matched the tetraCB, pentaCB, hexaCB, and heptaCB distribution of the other stations. ST005 (RM 6.0W), opposite ST004, had a relatively higher proportion of tetraCBs and pentaCBs, and lower abundance of heptaCBs compared to ST004. TriCBs made up a larger proportion of the samples from ST011 in Quarters 1 and 2 in comparison to other locations. The octaCB proportion appeared elevated in the Quarter 4 sample from this station. Quarter 3 and 4 samples from ST011 had total PCB congener concentrations 2 to 3 times higher than the Quarter 1 and 2 samples.

D2.3.3 Patterns and Trends of Total PCDD/Fs and TCDD TEQ in Mobile Sediment

Homolog patterns for sediment trap samples showed octachlorodibenzo-p-dioxin (OCDD) as the dominant homolog in almost all sediment trap samples, with heptachlorodibenzo-p-dioxins (HpCDDs) present to a substantial degree in most samples (Figures D2.3-5a-b). Polychlorinated dibenzofurans (PCDFs) generally accounted for less than about 20 percent of the total PCDD/Fs in most of the samples. Octachlorodibenzofuran (OCDF) typically accounted for the highest furan concentrations, followed by heptachlorodibenzofurans (HpCDFs).

Samples with homolog patterns apparently different from the prevailing pattern were observed at several locations during the 2006/2007 sampling event, but these patterns are obscured because U-qualifiers were applied during data validation in most cases; non-detects are treated as zero in the graphs of chemical patterns. However, the Quarter 2 sample from ST008 (RM 11.5W) was notable for its relatively high proportions of OCDF and relatively low proportions of OCDD compared to other samples.

The following samples from the 2006/2007 sampling event have incomplete PCDD/F patterns because some of the PCDD/F homolog data were qualified as not detected during validation (Anchor and Integral 2008): ST010, Quarter 2 (HpCDDs not detected) and Quarter 4 (HpCDFs and OCDF not detected); ST003 (Multnomah Channel), Quarter 2 (hexachlorodibenzo-p-dioxins [HxCDDs], hexachlorodibenzofurans [HxCDFs], HpCDDs, HpCDFs, and OCDD not detected); ST008, Quarter 4 (HpCDFs and OCDF not detected); and ST016 (RM 9.9E), Quarter 4 (HpCDFs not detected).

Toxic equivalent (TEQ) concentrations derived from PCDD/Fs closely track total PCDD/F homolog concentrations, both geographically and seasonally. The close parallel is due to the resemblance in homolog patterns among samples. TEQ

concentrations are generally 2 to 3 orders of magnitude lower than total PCDD/F homolog concentrations due to the abundance of higher chlorinated 2,3,7,8-substituted dioxins and furans, which have less toxic equivalency than tetra- and penta-chlorinated congeners.

D2.3.4 Patterns and Trends of DDx in Mobile Sediment

The relative concentration of DDD, DDE, and DDT varied widely among samples. Among the 2,4'- and 4,4'-isomers, the 4,4'-isomers generally predominated (Figures D2.3-6a-b). On average, 4,4'-DDT comprised the largest proportion of DDx in samples from the 2006/2007 sampling event, followed by 4,4'-DDE and 4,4'-DDD. Among the 2,4'-isomers, 2,4'-DDT was found at the highest percentage of DDx, followed by 2,4'-DDD and 2,4'-DDE. Among the 2009 samples, 4,4'-DDE generally comprised the largest portion of the DDx in samples where it was detected, followed by 2,4'-DDD and 2,4'-DDT.

During the 2006/2007 sampling event Stations ST007 and ST015 (RM 9.7E) had the highest proportion of 2,4'-DDx compounds due to comparatively high percentages of 2,4'-DDD and 2,4'-DDT. Station ST013 (RM 6.7W) also had a high percentage of 2,4'-DDT in the Quarter 4 sample. Upstream samples were primarily composed of 4,4'-DDx isomers.

The DDD isomers exhibited variability in both their concentration and relative contributions at most stations. No seasonal or geographic trends were evident during the 2006/2007 sampling event; however, 2,4'-DDD was dominant in the Quarter 3 2009 samples from ST001, ST002, and ST004 at RM 11E, and in both the Quarter 3 and 4 samples at ST003.

During the 2006/2007 sampling event DDT isomers appeared to have the highest relative concentrations during Quarter 1, although no geographical trends were apparent. A more seasonal trend was observed for DDE isomers, which were reported at detectable concentrations in all but two of the samples from Quarters 2 through 4, yet were detected in only 3 of the 13 samples from Quarter 1. Relative contributions of DDE compounds to DDx were generally highest during Quarter 4.

DDx at ST007 in Quarter 3 and 4 samples from the 2006/2007 sampling event (24 and 150 µg/kg, respectively) was composed entirely of 2,4'-DDD. However, 2,4'-DDD reported by the laboratory in these cases may be artifacts of PCB interference. High concentrations of Aroclor 1260 were also detected at this station in these samples (1,800 and 2,600 µg/kg, respectively). Aroclors have the potential to interfere with the analysis of DDx due to co-elution of Aroclor peaks with DDx compounds. While the 2,4'-DDD results were not N-qualified during data validation, the results for other isomers (2,4'-DDT and 4,4'-DDT in both Quarters 3 and 4, and 2,4'-DDE in Quarter 4) were N-qualified. It is possible that the reported results were affected by Aroclor interferences.

D2.3.5 Patterns and Trends of PAHs in Mobile Sediment

Paired samples from the 2006/2007 sampling event generally did not display substantial differences in total PAHs concentrations, with two notable exceptions. There were large differences between total PAHs concentrations at ST005 and its cross-river counterpart (ST004, RM 6.0E) during all quarters for which samples from both stations were analyzed. Total PAHs concentrations during Quarter 1 at ST010 were also higher than in the concurrent sample from ST009 (RM 15.7E).

An evaluation of the PAH composition among samples was done by combining the 17 individual PAH compounds into categories determined by their number of fused rings. Fused ring patterns did not appear to vary substantially among samples, with four-ring PAHs as the predominant component, followed by those with five rings (Figures D2.3-7a-b). High-molecular-weight polycyclic aromatic hydrocarbons (PAHs with four or more fused rings) generally accounted for more than 80 percent of total PAHs. A bar chart of all site PAHs (Figures D2.3-8a-b) shows that the four-ring PAHs consist primarily of fluoranthene and pyrene and the five-ring PAHs consist primarily of benzo(a)pyrene and benzo(b)fluoranthene.

The PAH distributions at ST005, the location with the highest total PAHs concentrations, were similar to the prevailing pattern. Samples with PAH distributions that appeared to differ somewhat from the prevailing pattern were observed during the 2006/2007 sampling event at several locations:

- The Quarter 2 sample from ST009 (RM 15.7E) exhibited apparent increased contributions from five-ring PAHs, mainly BAP.
- At ST002 (RM 1.8W), the Quarter 2 and 3 samples exhibited apparent increased contributions from five-ring and six-ring PAHs. However, the distribution of the individual PAHs within the five-ring and six-ring PAH groups appeared similar to other samples.
- At ST003 (Multnomah Channel), apparent increased contributions from five-ring and six-ring PAHs were observed in the Quarter 2 and 4 samples. The distribution of the individual PAHs within the five-ring and six-ring PAH groups appeared similar to other samples.

The evaluation of the low-molecular-weight polycyclic aromatic hydrocarbon (LPAH) distributions is confounded by the fact that eight results for naphthalene (a two-ring PAH) from Quarter 2 were restated as not detected because of laboratory blank results (Anchor and Integral 2008). The levels of LPAHs in these Quarter 2 samples may be under-represented. With that caveat, samples from Quarter 1 at ST010 (RM 15.6W), Quarter 3 at ST011 (RM 3.5E), and Quarter 4 at ST003 (Multnomah Channel)—all with total PAH concentrations greater than 1,000 $\mu\text{g/kg}$ (1,300 J $\mu\text{g/kg}$, 1,600 J $\mu\text{g/kg}$, and 2,700 J $\mu\text{g/kg}$, respectively)—are notable for their low contribution (less than 20 percent) of LPAHs to the total PAHs.

D2.3.6 Reference

Anchor and Integral. 2008. Portland Harbor RI/FS Round 3A In-River Sediment Trap Sampling Data Report. AE08-09. Prepared for the Lower Willamette Group, Portland, OR. Anchor Environmental, L.L.C., Seattle, WA, and Integral Consulting Inc., Mercer Island, WA. July 18, 2008.